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(54) Coloured cosmetic sticks of improved hardness

Gefärbte kosmetische Stifte mit verbesserter Härte

Bâtons cosmétiques colorés à dureté améliorée

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(56) References cited:
EP-A- 0 522 618 **FR-A- 2 356 411**
US-A- 4 695 452 **US-A- 5 108 737**

- **Section Ch, Week 7191, 20 August 1983 Derwent**
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182

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EP 0 545 715 B1

Description

The invention relates to a coloured cosmetic stick of improved rigidity in use, in particular lipstick compositions.

Traditional lipsticks are formulated with hydrophobic ingredients such as triglyceride or fatty acid ester derived oils and waxes. In particular, the waxes are important to impart the requisite stiffness or rigidity for structurant purposes.

A problem occasionally arises when a batch of lipstick inexplicitly turns too soft, thereby drawing the composition outside the hardness specification. Not only are these odd batches a quality control problem, but there is a direct negative impact upon production costs when an errant batch must be discarded. Causes of the problem have not been fully identified.

JP 58/09265 describes a lipstick of slightly improved fracture strength comprising beeswax in which the free fatty acid has been esterified.

It is now an object of the present invention to provide a coloured cosmetic stick, especially a lipstick, formulated with hydrophobic ingredients including oils and waxes which result in a product of reproducibly satisfactory hardness.

Another object of the present invention is to provide a coloured cosmetic stick, especially a lipstick, that can be rendered reproducibly hard in a cost efficient method.

A still further object of the present invention is to provide a coloured cosmetic stick, especially a lipstick, formulated with both yellow and red colorants that will have good colour impact while maintaining structural and aesthetic integrity.

These and other objects, features and advantages of the present invention will become more readily apparent through consideration of the following summary, detailed description and examples which follow.

It has now been found that traces of water, sometimes considerably less than 0.3% water, may adversely interact with colorants such as aluminum salts or lakes present in the composition which then further react with C₁₂-C₆₀ fatty acids to form aluminum soaps. These soaps act as crystal poisons which cause the stick to lose structure. Thus, compositions of the present invention should be formulated with less than an effective amount of the C₁₂-C₆₀ fatty acid that would otherwise form a soap with aluminum lakes. While fatty acids are not often purposely formulated with coloured cosmetic sticks, these materials are often present as substantial impurities in standard waxes such as candelilla, ozokerite, carnauba, beeswax, lanolin and spermaceti waxes.

Armed with this insight, a method has been devised for manufacturing coloured cosmetic sticks that insures reproducible hardness. The method comprises:

(i) selecting a wax that has been esterified with an alcohol to convert all naturally present C₁₂-C₆₀ fatty acid into a respective ester;

(ii) mixing the esterified wax in an amount from about 1 to about 99% with a colorant which is an aluminum salt in an amount from about 0.001 to about 20%; and

(iii) forming a coloured cosmetic stick with the mixture from step (ii).

According to the invention, there is provided a coloured cosmetic stick comprising

(i) from 1 to 99% by weight of a natural wax which is free from free C₁₂-C₆₀ fatty acids,

(ii) from 0.001 to 20% by weight of an aluminum salt colourant, and

(iii) from 0.001 to 20% by weight of a C₁₂-C₆₀ fatty acid ester,

the stick comprising less than 0.3% by weight of water.

Accordingly, there is provided the use in a cosmetic stick, in particular a lipstick, of a wax that has been esterified with an alcohol to convert all naturally present C₁₂-C₆₀ fatty acid in a respective ester, for the purpose of manufacturing a cosmetic stick of reproducible hardness.

The manufacture of a reproducibly rigid coloured cosmetic stick requires provision of a wax which is free from any C₁₂-C₆₀ fatty acid, especially fatty monocarboxylic acid, an impurity normally present in the natural waxes. This impurity may be counteracted through esterification with a molar equivalent or more of a C₁-C₆₀ mono or polyhydric alcohol. Particularly preferred are the C₁-C₆₀ monohydric alcohols. Illustrative alcohols useful herein include methanol, ethanol, lauryl alcohol, palmitic alcohol and combinations thereof.

The esterification process involves combining the natural wax with from 0.5 to 20% of the alcohol in a vessel under agitation at a temperature of anywhere from about 40°C to about 250°C, preferably from about 80°C to about 150°C.

Advantageously, a vacuum is applied to the vessel to remove water vapour formed in the esterification. An effective amount of a Lewis acid catalyst may be employed, for instance, a mineral acid (e.g. sulfuric or hydrochloric acid), an organic acid (e.g. toluene sulfonic acid) or an inorganic substance such as boron trifluoride etherate.

The natural waxes suitable for the present invention are normally low-melting organic compounds of high molecular weight, solid at room temperature and generally similar in composition to fats and oils, except that they contain no glycerides. Waxes are thermoplastic, but since they are not high polymers, they are not considered in the family of plastics. Among the natural waxes are those of animal origin (beeswax, spermaceti, lanolin, shellac wax) and vegetable origin (carnauba, candelilla, bayberry, sugarcane wax). Most preferred are candelilla, carnauba, beeswax, lanolin and spermaceti waxes.

Amounts of the wax may range anywhere from about 1 to about 99% by weight, preferably from about 10 to about 50%, optimally between about 15 and about 25% by weight.

Compositions of the present invention will contain from about 0.001 to about 20% by weight of a colorant which is an aluminum salt. Amounts of colorant will preferably range from about 0.1 to about 10%, optimally from about 0.5 to about 8% by weight.

Advantageously, the aluminum salt is an aluminum lake. Lakes are either a pigment that is extended or reduced with a solid diluent or an organic pigment that is prepared by the precipitation of a water-soluble dye on an adsorptive surface, which usually is alumina hydrate. There is uncertainty in some instances as to whether the soluble dye precipitates on the surface of the alumina hydrate to yield a dyed inorganic pigment or whether it merely precipitates in the presence of the substrate. A lake also forms from precipitation of an insoluble salt from an acid or basic dye.

Particularly preferred aluminum lakes of the present invention are Red 3 Aluminum Lake, Red 21 Aluminum Lake, Red 27 Aluminum Lake, Red 28 Aluminum Lake, Red 33 Aluminum Lake, Yellow 5 Aluminum Lake, Yellow 6 Aluminum Lake, Yellow 10 Aluminum Lake, Orange 5 Aluminum Lake and Blue 1 Aluminum Lake.

Beyond the basic components of the present invention, there optionally may be other ingredients which serve to enhance product function and aesthetics. These optional ingredients are detailed below.

Emulsifiers may be incorporated in the cosmetic formulations of the present invention. Overall concentration of emulsifier may range anywhere from about 0.1 to about 30% by weight of the formulation, preferably from about 0.5 to about 20%, optimally between about 2 and 10% by weight.

Phospholipids is an important category of emulsifiers that may contribute to the stability and pleasing appearance of the composition.

Examples of phospholipids are those within the categories of phosphoglycerides, lysophosphoglycerides, sphingomyelins and mixtures thereof. Especially useful as a phospholipid is lecithin.

Fatty acid derivative-type emulsifiers may also be employed, especially in combination with a phospholipid. These emulsifiers may include monoacyl glycerol, diacyl glycerol and polyglycerol esters and combinations thereof. Especially preferred are glycerol monoalkanoates, an example of which are the monoglycerides of sunflower seed oil and of palm oil.

Emollient oils which are defined as oily organic substances liquid at room temperature (i.e. 20°C) can be employed singly or as mixtures of two or more oils. They normally will be present at levels from about 2 to about 97%, preferably from about 30 to 70% by weight of the composition.

These oils are useful not only for emollient purposes but may also impart viscosity, tackiness and drag properties. Examples of suitable oils include caprylic triglycerides; capric triglycerides; isostearic triglycerides; adipic triglycerides; propylene glycol myristyl acetate; lanolin oil; polybutene; isopropyl palmitate; isopropyl myristate; diethyl sebacate; diisopropyl adipate; hexadecyl stearate; cetyl oleate; oleyl alcohol; hexadecyl alcohol; wheatgerm oil; hydrogenated vegetable oils; petrolatum; modified lanolins; branched-chain hydrocarbons, alcohols and esters; castor oil; corn oil; cottonseed oil; olive oil; palm kernel oil; rapeseed oil; safflower seed oil; jojoba oil; evening primrose oil; avocado oil; mineral oil; and volatile and non-volatile silicone oils.

Skin active ingredients in the form of both water-soluble and insoluble substances may be included within the formulations of this invention. These ingredients may range anywhere from about 0.0001 to about 10% by weight. Examples include zinc oxide; b-glycyrrhetic acid; chamomile oil; ginkgo biloba extract; pyroglutamic acid, salts or esters; sodium hyaluronate; 2-hydroxyoctanoic acid; sulphur; salicylic acid; carboxymethyl cysteine and mixtures thereof.

The following examples will more fully illustrate certain aspects of the present invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE

Beeswax containing free fatty acids was heated along with a C₁₄-C₁₆ alcohol mixture to 200°C under a vacuum of approximately 7 inches for approximately three hours. Lipsticks were prepared having the following formula:

Ingredient	% Weight
Castor oil	19.5
Isopropyl palmitate	11.6
Caprylic/capric/isostearic/adipic triglyceride	7.0
Lanolin	7.0
Red 21 Aluminum Lake	7.0
Candelilla wax	6.6
Propylene glycol myristyl ether acetate	6.0
Caprylic/capric triglyceride	5.8
Glycerol	5.0
Water	5.0
Titanium dioxide	4.7
Beeswax	4.1
Monoglyceride	3.5
Lanolin oil	2.5
Ozokerite wax	2.5
Phospholipid (soybean lecithin)	1.0
Polybutene	0.8
Carnauba wax	0.4

Lipsticks similar in composition to those above were formulated with the waxes still retaining their free fatty acid impurities ("Non-Esterified"). Other sticks were formed from the same waxes that were, however, esterified.

Table I describes the results of various physical property tests on both sets of lipsticks.

Table I

Rheological and Stability Results			
	Crush (g)	Break (g)	Phase Stability
Esterified Waxes exudation	3,200.0	425.0	No oil
Non Esterified exudation	600	200	Oil

Phase stability was measured by a freeze/thaw test. Samples of the lipstick were subjected to freeze/thaw cycling between 0°C/45°C, 40°C and room temperature. Crush and break measurements were obtained on a Chatillion apparatus.

An acceptable lipstick normally will have crush and break values of greater than 2,000g and 400g, respectively. Only the esterified wax formula provided acceptable crush, break and stability values. There was also a quite noticeable increase in surface gloss in the formulas containing esterified waxes which is an indication of relatively good crystalline structure.

Claims

1. A coloured cosmetic stick comprising from 1 to 99% by weight of a natural wax which is free from free C₁₂-C₆₀ fatty acids characterised in that the stick comprises

(i) from 0.001 to 20% by weight of an aluminum salt colourant, and

(ii) from 0.001 to 20% by weight of a C₁₂-C₆₀ fatty acid ester the stick comprising less than 0.3% by weight of water.

2. A coloured cosmetic stick according to claim 1 wherein the aluminum salt is an aluminum lake.

3. A coloured cosmetic stick according to claim 1 or claim 2 the aluminum salt comprises Red 3 Aluminum Lake, Red 21 Aluminum Lake, Red 27 Aluminum Lake, Red 28 Aluminum Lake, Red 33 Aluminum Lake, Yellow 5 Aluminum Lake, Yellow 6 Aluminum Lake, Yellow 10 Aluminum Lake, Orange 5 Aluminum Lake, Blue 1 Aluminum Lake or mixtures thereof.

4. A coloured cosmetic stick according to any one of the preceding claims wherein the wax comprises candelilla, carnauba, beeswax, lanolin, spermaceti or wax mixtures thereof.

5. A coloured cosmetic stick according to any one of the preceding claims wherein the wax is present in an amount of from 10 to 50% by weight.

Patentansprüche

1. Gefärbter kosmetischer Stift, umfassend 1 bis 99 Gewichtsprozent eines natürlichen Wachses, das frei von freien C₁₂-C₆₀-Fettsäuren ist, dadurch gekennzeichnet, daß der Stift umfaßt

(i) 0,001 bis 20 Gewichtsprozent eines Aluminiumsalz-Färbemittels und

(ii) 0,001 bis 20 Gewichtsprozent eines C₁₂-C₆₀-Fettsäureesters, wobei der Stift weniger als 0,3 Gewichtsprozent Wasser umfaßt.

2. Gefärbter kosmetischer Stift nach Anspruch 1, wobei das Aluminiumsalz ein Aluminiumlack ist.

3. Gefärbter kosmetischer Stift nach Anspruch 1 oder Anspruch 2, wobei das Aluminiumsalz Red 3 Aluminum Lake, Red 21 Aluminum Lake, Red 27 Aluminum Lake, Red 28 Aluminum Lake, Red 33 Aluminum Lake, Yellow 5 Aluminum Lake, Yellow 6 Aluminum Lake, Yellow 10 Aluminum Lake, Orange 5 Aluminum Lake, Blue 1 Aluminum Lake oder Gemische davon umfaßt.

4. Gefärbter kosmetischer Stift nach einem der vorangehenden Ansprüche, wobei das Wachs Candelilla-, Carnauba-, Bienenwachs, Lanolin, Walrat oder Wachsgemische davon umfaßt.

5. Gefärbter kosmetischer Stift nach einem der vorangehenden Ansprüche, wobei das Wachs in einer Menge von 10 bis 50 Gewichtsprozent vorliegt.

Revendications

1. Bâton cosmétique coloré comprenant de 1 à 99% en poids d'une cire naturelle qui est exempte d'acides gras libres en C₁₂₋₆₀, caractérisé en ce que le bâton comprend :

(i) de 0,001 à 20% en poids d'un colorant de sel d'aluminium et

(ii) de 0,001 à 20% en poids d'un ester d'acide gras en C₁₂₋₆₀,

le bâton comprenant moins de 0,3% en poids d'eau.

2. Bâton cosmétique coloré selon la revendication 1, dans lequel le sel d'aluminium est une laque d'aluminium.

3. Bâton cosmétique coloré selon la revendication 1 ou 2, dans lequel le sel d'aluminium consiste en Laque d'aluminium RED 3, Laque d'aluminium RED 21, Laque d'aluminium RED 27, Laque d'aluminium RED 28, Laque d'aluminium RED 33, Laque d'aluminium YELLOW 5, Laque d'aluminium YELLOW 6, Laque d'aluminium YELLOW 10, Laque d'aluminium ORANGE 5 et Laque d'aluminium BLUE 1 ou leurs mélanges.

EP 0 545 715 B1

4. Bâton cosmétique coloré selon l'une quelconque des revendications précédentes, dans lequel la cire comprend la cire de candelilla, carnauba, la cire d'abeille, la lanoline, le spermaceti ou leurs mélanges.
5. Bâton cosmétique coloré selon l'une quelconque des revendications précédentes, dans lequel la cire est présente en une quantité de 10 à 50% en poids.

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